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Patentanmeldung Nr.
Patent application no.
Demande de brevet n°

PCT/EP 02/14717

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PCT/EP 02/14717

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TYRE FOR TWO - WHEELED VEHICLES

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TYRE FOR TWO-WHEELED VEHICLES

The present invention relates to a tyre for two-wheeled vehicles.

5 More particularly, the present invention relates to a tyre for two-wheeled vehicles comprising at least one layer of a crosslinked elastomeric material comprising at least one layered inorganic material.

10 The present invention moreover relates to a process for manufacturing said tyre.

In the field of production of tyres for two-wheeled vehicles, in particular those intended for equipping the so-called high-performance "touring" motorcycles or the race motorcycles, the need is increasingly felt of providing ever higher performances in terms of road behaviour both in straight stretch and in cornering, stability of the vehicle at high speed, kilometric yield, wear uniformity and regularity, and low weight.

20 Said tyres are characterized by a high transverse curvature in order to provide good contact with the road surface when the motorcycles are steeply banked in cornering. Maintenance of a consistent ground contact area of "tyre footprint" under all conditions is a major problem in determining general vehicle handling.

25 Of particular importance, particularly in race motorcycles tyres, is the provision of high cornering power along with good stability to maximise cornering speeds under race conditions and the maintenance of tyre shape and foot-print under conditions of heavy braking.

30 Attempts have been made in the prior art in order to satisfy the above reported needs.

For example, European Patent Application EP 703 102 relates to a motorcycle tyre comprising a tread reinforced between its edges by a breaker assembly and having in its normal inflated fitted condition a camber value C/L of between 0.5 and 0.7, a reinforcing carcass

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ply of rubber covered cords radially inside the breaker assembly and extending between two bead regions and wrapped in each bead region around an annular bead wire to form carcass ply turn-ups and between the tread edges and bead regions, tyre sidewalls, characterized in that under the tread is disposed radially inward of the breaker assembly a secondary carcass ply of rubber covered cords and between the carcass ply and the secondary carcass ply is disposed a rubber member extending from tread edge to tread edge. The resultant tyres would have not only an improved cornering power, damping and grip but also they would be stable and able to effectively resist collapse under severe breaking.

British Patent Application GB 2 283 215 relates to a radial motorcycle tyre comprising a tread reinforced between its edges by a breaker assembly and a bandage and having in its normally inflated condition a camber value C/L of between 0.5 to 0.7, a reinforcing carcass ply of radially disposed cords extending radially inside the breaker assembly and between two bead regions and wrapped in each bead region around an annular bead wire from the axial inside to the outside to form carcass ply turn-ups and between the tread edges and bead regions, tyre sidewalls, characterized in that the breaker assembly comprises two breaker plies comprising aromatic polyamide cords oppositely inclined at between 16 and 30 degrees with respect to the circumferential direction of the tyre and the bandage comprises nylon cords reinforced material, e.g. up to eight nylon cords side by side, and is formed radially outside and adjacent to the breaker assembly and is inclined at less than 5 degrees to the circumferential direction. The resultant tyres would have improved cornering power and stability under all conditions and improved grip. This tyre would show also superior fatigue life.

US Patent 6 412 533 relates to a tyre comprising:

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- a) a carcass structure including at least one ply provided with reinforcing cords essentially parallel to one another and oriented along directions inclined with respect to the equatorial plane of the tyre;
- 5 b) a belt structure coaxially extending around the carcass structure, including:
- 10 i) a radially inner layer comprising at least one sheet made of an elastomeric material;
- ii) a radially outer layer including a plurality of circumferential coils, axially arranged side by side, of at least one inextensible cord, circumferentially wound at a substantially null angle with respect to the equatorial plane of the tyre;
- 15 c) a tread coaxially extending around the belt structure.

Preferably, said sheet made of an elastomeric material incorporates appropriate binding means suitable to increase its stretchability properties without substantially altering the adhesion properties of the elastomeric material in the green state. More preferably, said binding means comprise the so-called aramid pulp (short fibrillated fibers of poly-paraphenylene-terephthalamide), of the type commercially known as "Kevlar"-pulp from DuPont or "Twaron"-pulp from Akzo. Preferably, said short fibrillated fibers are preoriented, for instance by means of a calendering operation, according to the main direction of the forces which the supporting element is subjected during the tyre manufacturing process. Such direction is usually the circumferential direction of the tyre and said preorientation is preferably carried out by calendering said sheet during its manufacture. By interposing a sheet made of an elastomeric material between the carcass structure and the radially outer layer provided

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with zero-degree cords of the belt structure, it would be possible to achieve at the same time both the desired features of road holding and curve stability imparted to the tyre by the carcass structure, and the desired features of confort, wear regularity and uniformity and stability of the vehicle at high speeds in straight stretches, imparted to the tyre by the zero-degree cord layer of the belt structure.

The Applicant has noticed that, the use of a layer made of an elastomeric material comprising short fibrillated fiber of poly-paraphenylene-terephthalamide associated with the belt structure as disclosed above, gives to the motorcycle tyre essentially a longitudinal reinforcement (e.g. said reinforcement is essentially in the circumferential direction of the tyre). However, according to the Applicant, a transversal reinforcement is also important to achieve a reliable behaviour of the motorcycle tyre, particularly during bending when the tyre is subjected to remarkable transversal forces.

The Applicant has now found that it is possible to give an effective reinforcement, both in longitudinal and in transversal direction, under the tread of a motorcycle tyre, by using at least one layer of a crosslinked elastomeric material comprising at least one layered inorganic material, associated with a belt structure.

According to a first aspect, the present invention thus relates to a tyre for two-wheeled vehicles, comprising:

- 30 - a carcass structure with at least one carcass ply shaped in a substantially toroidal configuration, the opposite lateral edges of which are associated with respective right-hand and left-hand bead wires, each bead wire being enclosed in a respective bead;
- 35 - a belt structure applied in a circumferentially external position relative to said carcass

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- structure;
- a tread band superimposed circumferentially on said belt structure;
 - a pair of side walls applied laterally on opposite sides relative to said carcass structure;
- 5 wherein said belt structure is associated with at least one layer of a crosslinked elastomeric material comprising:
- (a) at least one diene elastomeric polymer;
 - 10 (b) at least one layered inorganic material having an individual layer thickness of from 0.01 nm to 30 nm, preferably from 0.05 nm to 15 nm.
- Preferably, said belt structure comprises:
- 15 (i) at least one layer of a plurality of circumferential coils, axially arranged side by side, of at least one cord wound at substantially-null angle with respect to the equatorial plane of the tyre; or
 - 20 (ii) two layers of cords oriented according to two preferred directions crossing each other in the two layers and preferably symmetrically inclined in relation to the equatorial plane of the tyre; or
 - 25 (iii) a combination of (i) and (ii).
- According to one preferred embodiment, said at least one layer of a crosslinked elastomeric material is placed between said carcass structure and said belt structure.
- According to a further preferred embodiment, said at least one layer of a crosslinked elastomeric material is placed between said tread band and said belt structure.
- According to a further aspect, the present invention relates to a process for producing a tyre for two-wheeled vehicles, said process comprising the following
- 35 steps:
- manufacturing a green tyre by assembling at least

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- one carcass ply, a belt structure in a circumferentially outer position with respect to said carcass ply, a tread in a circumferentially outer position with respect to said belt structure;
- 5 - subjecting the green tyre to moulding in a mould cavity formed in a vulcanization mould;
- subjecting said green tyre to crosslinking by heating;

10 said process further comprising the step of associating at least one layer of a crosslinkable elastomeric material with said belt structure, said elastomeric material comprising:

- (a) at least one diene elastomeric polymer;
- (b) at least one layered inorganic material having an individual layer thickness of from 0.01 nm to 30 nm,
- 15 preferably from 0.05 nm to 15 nm.

According to a further preferred embodiment, said at least one layer of a crosslinkable elastomeric material is obtained by winding at least one ribbon-like band consisting of said crosslinkable elastomeric material in side by side coils. Said ribbon-like band may be produced, for example, by extruding said crosslinkable elastomeric material. Further details of the methods of forming and/or depositing the various components of the tyre on a toroidal support are described, for example,

20 in International Patent application WO 01/36185 and in European Patent EP 976 536 in the name of the same Applicant.

According to one preferred embodiment, said layered inorganic material (b) is intercalated in the elastomeric material.

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According to a further preferred embodiment, said inorganic material (b) is exfoliated in the elastomeric material.

35 For the purposes of the present description and of the claims which follows, the term "intercalated in the

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elastomeric material" means that the diene elastomeric polymer (a) is disposed between the layers of the layered inorganic material (b) so as to form a nanocomposite of ordered multilayers with alternating polymer/inorganic layers.

For the purposes of the present description and of the claims which follows, the term "exfoliated in the elastomeric material" means that a nanocomposite is formed wherein the layers of said layered inorganic material (b) are individually dispersed throughout the elastomeric material.

The structure of the layered inorganic material (b) may be determined by using X-ray diffraction (XRD) or transmission electron microscopy (TEM). More information about both the morphology and the characterization of said layered inorganic material may be found, for example, in: "Polymer-Silicate Nanocomposites: Model Systems for Confined Polymers and Polymer Brushes", E.P. Giannelis, R. Krishnamoorti, E. Manias, Advances in Polymer Science (1999), Vol. 138, Springer-Verlag, Berlin, Heidelberg, pg.107-147

According to one preferred embodiment, said layered inorganic material (b) exhibits, in the elastomeric material, a d-spacing value in X-ray diffraction analysis of at least 10% higher, preferably of at least 20% higher, with respect to the d-spacing value of the layered inorganic material (b) before dispersing it into the diene elastomeric polymer (a).

For the purpose of the present invention, the variations (%) of the d-spacing values in X-ray diffraction analysis have been calculated as follows. The analysis was carried out by inserting the test samples (the samples were obtained in the manner described in the examples given below) in a Philips Xpert diffractometer, employing analysis radiation of the CuK α type. The data were obtained with a step of

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0.04°2θ and a count of 6 seconds per step in the range 1.4°2θ-32.0°2θ. The d-spacing value was calculated using the following formula:

$$d\text{-spacing} = \lambda / 2 \sin \theta$$

- 5 in which λ is the wavelength of the $K\alpha$ radiation of Cu (average of $K\alpha_1$ and $K\alpha_2$) equal to 1.54178 Å.

The d-spacing value corresponds to the value of the distance between the crystal planes of the layered inorganic material (b) in the elastomeric material, in particular said value is the average distance between the corresponding surfaces of contiguous layers of the layered inorganic material. The effective distance between the continuous layers is obtained by subtracting the thickness of the individual layer from the d-spacing value.

15 According to one preferred embodiment, said layered inorganic material (b) is present in the elastomeric material in an amount of from 1 phr to 120 phr, preferably from 5 phr to 80 phr.

20 For the purposes of the present description and of the claims which follows, the term "phr" means the parts by weight of a given component of the elastomeric material per 100 parts by weight of the diene elastomeric polymer.

25 According to one preferred embodiment, said at least one layer of elastomeric material has a thickness of between 0.075 mm and 5 mm, preferably between 0.4 mm and 3 mm.

30 According to one preferred embodiment, said elastomeric material further comprises at least one silane coupling agent (c).

According to one preferred embodiment, the layered inorganic material (b) which may be used in the present invention may be selected, for example, from
35 phyllosilicates such as: smectites, for example, montmorillonite, nontronite, beidellite, volkonskoite,

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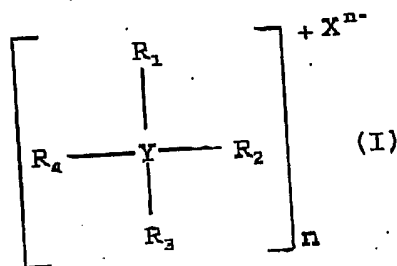
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hectorite, saponite, sauconite; vermiculite; halloisite; sericite; or mixtures thereof. Montmorillonite is particularly preferred.

- In order to render the layered inorganic material
- 5 (b) more compatible with the diene elastomeric polymer
- (a) said layered inorganic material may be surface-treated with a compatibilizer.

According to one preferred embodiment, said compatibilizer may be selected, for example, from the

10 quaternary ammonium or phosphonium salts having general formula (I):



wherein:

- Y represents N or P;
- 15 - R_1 , R_2 , R_3 and R_4 , which may be identical or different, represent a linear or branched C_1 - C_{20} alkyl or hydroxyalkyl group; a linear or branched C_1 - C_{20} alkenyl or hydroxyalkenyl group; a group $-R_5$ -SH or R_5 -NH wherein R_5 represents a linear or branched C_1 - C_{20} alkylene group; a C_5 - C_{18} aryl group; a
- 20 C_7 - C_{20} arylalkyl or alkylaryl group; a C_5 - C_{18} cycloalkyl group, said cycloalkyl group possibly containing hetero atom such as oxygen, nitrogen or sulphur;
- 25 - X^{n-} represents an anion such as the chlorine ion, the sulphate ion or the phosphate ion;
- n represents 1, 2 or 3.

Example of layered inorganic material (b) which may be used according to the present invention and is

30 available commercially is the product known by the name of Dellite® 67G from Laviosa Chimica Mineraria S.p.A.

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According to one preferred embodiment, the diene elastomeric polymer (a) which may be used in the present invention may be selected from those commonly used in sulphur-crosslinkable elastomeric compositions, that are particularly suitable for producing tyres, that is to say from elastomeric polymers or copolymers with an unsaturated chain having a glass transition temperature (T_g) generally below 20°C , preferably in the range of from 0°C to -90°C . These polymers or copolymers may be of natural origin or may be obtained by solution polymerization, emulsion polymerization or gas-phase polymerization of one or more conjugated diolefins, optionally blended with at least one comonomer selected from monovinylarenes and/or polar comonomers in an amount of not more than 60% by weight.

The conjugated diolefins generally contain from 4 to 12, preferably from 4 to 8 carbon atoms, and may be selected, for example, from the group comprising: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 3-butyl-1,3-octadiene, 2-phenyl-1,3-butadiene, or mixtures thereof. 1,3-butadiene and isoprene are particularly preferred.

Monovinylarenes which may optionally be used as comonomers generally contain from 8 to 20, preferably from 8 to 12 carbon atoms, and may be selected, for example, from: styrene; 1-vinylnaphthalene; 2-vinylnaphthalene; various alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl derivatives of styrene such as, for example, α -methylstyrene, 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzylstyrene, 4-p-tolylstyrene, 4-(4-phenylbutyl)styrene, or mixtures thereof. Styrene is particularly preferred.

Polar comonomers which may optionally be used may be selected, for example, from: vinylpyridine, vinylquinoline, acrylic acid and alkylacrylic acid

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esters, nitriles, or mixtures thereof, such as, for example, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylonitrile, or mixtures thereof.

- 5 Preferably, the diene elastomeric polymer (a) which may be used in the present invention may be selected, for example, from: cis-1,4-polyisoprene (natural or synthetic, preferably natural rubber), 3,4-polyisoprene, polybutadiene (in particular polybutadiene with a high
- 10 1,4-cis content), optionally halogenated isoprene/isobutene copolymers, 1,3-butadiene/acrylonitrile copolymers, styrene/1,3-butadiene copolymers, styrene/isoprene/1,3-butadiene copolymers, styrene/1,3-butadiene/acrylonitrile
- 15 copolymers, or mixtures thereof.

- The elastomeric material according to the present invention may optionally comprise at least one elastomeric polymer of one or more monoolefins with an olefinic comonomer or derivatives thereof (a'). The
- 20 monoolefins may be selected from: ethylene and α -olefins generally containing from 3 to 12 carbon atoms, such as, for example, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, or mixtures thereof. The following are preferred: copolymers between ethylene and an α -olefin,
- 25 optionally with a diene; isobutene homopolymers or copolymers thereof with small amounts of a diene, which are optionally at least partially halogenated. The diene optionally present generally contains from 4 to 20 carbon atoms and is preferably selected from: 1,3-
- 30 butadiene, isoprene, 1,4-hexadiene, 1,4-cyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, vinylnorbornene, or mixtures thereof. Among these, the following are particularly preferred: ethylene/propylene copolymers (EPR) or ethylene/propylene/diene copolymers
- 35 (EPDM); polyisobutene; butyl rubbers; halobutyl rubbers, in particular chlorobutyl or bromobutyl rubbers; or

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mixtures thereof.

A diene elastomeric polymer (a) or an elastomeric polymer (a') functionalized by reaction with suitable terminating agents or coupling agents may also be used.

5 In particular, the diene elastomeric polymers obtained by anionic polymerization in the presence of an organometallic initiator (in particular an organolithium initiator) may be functionalized by reacting the residual organometallic groups derived from the

10 initiator with suitable terminating agents or coupling agents such as, for example, imines, carbodiimides, alkyltin halides, substituted benzophenones, alkoxysilanes or aryloxysilanes (see, for example, European patent EP 451 604, or patents US 4 742 124 and

15 US 4 550 142).

As disclosed above, the elastomeric material according to the present invention further comprises at least one silane coupling agent (c).

According to one preferred embodiment, the silane

20 coupling agent (c) which may be used in the present invention may be selected from those having at least one hydrolyzable silane group which may be identified, for example, by the following structural formula (II):



25 in which the groups R, which may be identical or different, are selected from: alkyl, alkoxy or aryloxy groups or from halogen atoms, on condition that at least one of the groups R is an alkoxy or aryloxy group; n is an integer between 1 and 6 inclusive; X is a group

30 selected from: nitroso, mercapto, amino, epoxide, vinyl, imide, chloro, $-(S)_mC_nH_{2n}-Si-(R)_3$ in which m and n are integers between 1 and 6 inclusive and the groups R are defined as above.

Among the coupling agents that are particularly

35 preferred are bis(3-triethoxysilylpropyl) tetrasulphide and bis(3-triethoxysilylpropyl) disulphide. Said

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coupling agents may be used as such or as a suitable mixture with an inert filler (for example carbon black) so as to facilitate their incorporation into the elastomeric material.

5 According to one preferred embodiment, said coupling agent (c) is present in the elastomeric material in an amount of from 0.01 phr to 10 phr, preferably from 0.5 phr to 5 phr.

10 At least one additional reinforcing filler may advantageously be added to the elastomeric material according to the present invention, in an amount generally of from 0.1 phr to 120 phr, preferably from 20 phr to 90 phr. Preferably, the total amount of said at least one additional reinforcing filler and the layered
15 inorganic material (b) is not higher than 120 phr. The reinforcing filler may be selected from those commonly used for crosslinked manufactured products, in particular for tyres, such as, for example, carbon black, silica, alumina, aluminosilicates, calcium
20 carbonate, kaolin, or mixtures thereof.

The types of carbon black which may be used according to the present invention may be selected from those conventionally used in the production of tyres, generally having a surface area of not less than 20 m²/g
25 (determined by CTAB absorption as described in ISO standard 6810).

The silica which may be used according to the present invention may generally be a pyrogenic silica or, preferably, a precipitated silica, with a BET
30 surface area (measured according to ISO standard 5794/1) of from 50 m²/g to 500 m²/g, preferably from 70 m²/g to 200 m²/g.

When a reinforcing filler comprising silica is present, the elastomeric material may advantageously
35 incorporate at least one silane coupling agent (c) capable of interacting with the silica and of linking it

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to the diene elastomeric polymer during the vulcanization. Examples of silane coupling agent (c) which may be used have been already disclosed above.

The elastomeric material according to the present invention may be vulcanized according to known techniques, in particular with sulphur-based vulcanizing systems commonly used for diene elastomeric polymers.

The vulcanizing agent most advantageously used is sulphur, or molecules containing sulphur (sulphur donors), with accelerators and activators known to those skilled in the art.

Activators that are particularly effective are zinc compounds, and in particular ZnO , $ZnCO_3$, zinc salts of saturated or unsaturated fatty acids containing from 8 to 18 carbon atoms, such as, for example, zinc stearate, which are preferably formed in situ in the elastomeric material from ZnO and fatty acid, and also BiO , PbO , Pb_3O_4 , PbO_2 , or mixtures thereof.

Accelerators that are commonly used may be selected from: dithiocarbamates, guanidine, thiourea, thiazoles, sulphenamides, thiurams, amines, xanthogenates, or mixtures thereof.

The elastomeric material according to the present invention may comprise other commonly used additives selected on the basis of the specific application for which the composition is intended. For example, the following may be added to said composition: antioxidants, anti-ageing agents, adhesives, anti-ozone agents, modifying resins, fibres (for example Kevlar® pulp), or mixtures thereof.

In particular, for the purpose of further improving the processability, a plasticizer generally selected from mineral oils, vegetable oils, synthetic oils, or mixtures thereof, such as, for example, aromatic oil, naphthenic oil, phthalates, soybean oil, or mixtures thereof, may be added to the elastomeric material

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according to the present invention. The amount of plasticizer generally ranges from 1 phr to 100 phr, preferably from 5 phr to 50 phr.

The elastomeric material according to the present invention may be prepared by mixing together the diene elastomeric polymer (a) with the layered inorganic material (b), with the additional reinforcing filler and with the other additives optionally present, according to techniques known in the art. The mixing may be carried out, for example, using an open mixer of open-mill type, or an internal mixer of the type with tangential rotors (Banbury) or with interlocking rotors (Intermix), or using continuous mixers of Ko-Kneader type (Buss), or using co-rotating or counter-rotating twin-screw extruders or single-screw extruders.

The present invention will now be illustrated in further detail by means of a number of illustrative embodiments, with reference to the attached Fig. 1-2, which are a view in cross section of a tyre made according to different embodiments of the present invention.

A high-transverse-curvature tyre for two-wheeled vehicles according to the invention has been generally identified by reference number (1).

With reference to Fig. 1, X-X indicates the equatorial plane of the tyre (1).

The tyre (1) comprises a carcass structure (2) comprising at least one carcass ply (3), the opposite lateral edges (3a) of which are associated with respective bead wires (4). The association between the carcass ply (3) and the bead wires (4) is achieved here by folding back the opposite lateral edges (3a) of the carcass ply (3) around the bead wires (4) so as to form the so-called carcass back-folds (3a) as shown in Fig.

35 1.

Alternatively, the conventional bead wires (4) can

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be replaced with at least one circumferentially inextensible annular insert formed from elongate element arranged in concentric coils (not represented in Fig. 1) (see, for example, European Patent EP 976 536 and International Patent Application WO 01/54926). In this case, the carcass ply (3) is not back-folded around said annular inserts, the coupling being provided by a second carcass ply (not represented in Fig. 1) applied externally over the first.

The carcass ply (3) generally consists of a plurality of reinforcing cords arranged parallel to each other and at least partially coated with a layer of elastomeric material. These reinforcing cords are usually made of textile fibres, for example rayon, nylon, polyethylene naphthalene-2,6-dicarboxylate (PEN), polyethylene terephthalate (PET), or of steel wires stranded together, coated with a metal alloy (for example copper/zinc, zinc/manganese, zinc/molybdenum/cobalt alloys and the like).

According to a preferred embodiment, the carcass structure (2) is of radial type, i.e. the carcass ply (3) incorporates reinforcing cords arranged in a substantially perpendicular direction relative to a circumferential direction.

Alternatively, the carcass structure (2) comprises a couple of radially inner and radially outer carcass plies (not represented in Fig. 1). In this case, the reinforcing cords are essentially parallel to one another and oriented according to inclined directions in each ply and opposed with respect to the cords of the adjacent ply with respect to the equatorial plane X-X of the tyre (1).

On the external peripheral edge of bead wires (4), an elastomeric filler (5) is applied which fills the space defined between the carcass structure (2) and the corresponding carcass back-folds (3a).

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As known, the tyre area comprising bead wires (4) and elastomeric filler (5) forms the so-called bead, globally indicated as (10), intended for anchoring the tyre (1) onto a corresponding mounting rim (not shown in Fig. 1).

A belt structure (6) is applied along the circumference of the carcass structure (2). The belt structure (6) comprises one layer including a plurality of circumferential coils (7a), axially arranged side by side, of a rubberized cord (7) or of a strip of a few rubberized cords (preferably 2 to 5), spirally wound at substantially-null angle from one end to the other of the carcass structure (2). The cords (7) form a plurality of circumferential coils (7a), substantially oriented according to the rolling direction of the tyre, usually called "zero-degree" arrangement with reference to its position with respect to the equatorial plane X-X the tyre (1).

Preferably, the circumferential coils are wound on the carcass structure (2) according to variable pitch so as to obtain, preferably, a cord thickness higher at opposite side portions than in the central portion of the belt structure (6).

Even though the spiralling by itself and any pitch variability involve a winding angle different from zero, this angle remains so small that it may substantially be considered as always equal to zero degrees.

Usually said cords (7) are textile or metal cords. Preferably, said cords (7) are steel cords, more preferably high elongation (HE) steel cords (see, for example, European Patent EP 461 646).

Preferably, such cords are made of high-carbon (HT) steel wires, i.e. steel wires with a carbon content higher than 0.9%.

When textile cords are used, they may be nylon, rayon, polyethylene naphthalene-2,6-dicarboxylate (PEN),

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polyethylene terephthalate (PET). Alternatively, hybrid cords may be used, constituted by at least one low modulus yarn (e.g. nylon or rayon) twisted with at least one high modulus yarn (e.g. aramide fibres such as, for example, Kevlar[®]).

Different techniques for winding the cords around the carcass are well known in the art such as disclosed, for example, in the above reported European Patent EP 461 646.

A side wall (11) is also applied externally onto the carcass ply (3), this side wall extending, in an axially external position, from the bead (10) to the end of the belt structure (5).

A tread band (8), whose lateral edges are connected to the side walls (11), is applied circumferentially in a position radially external to the belt structure (5). Externally, the tread band (8), has a rolling surface (8a) designed to come into contact with the ground by means of grooves of various shape so as to define a plurality of blocks of various shapes and sizes distributed over the rolling surface (8a).

In Fig. 1, a layer of a crosslinked elastomeric material (9) according to the present invention, is placed between the belt structure (7) and the carcass ply (3). In Fig. 1, said layer (9) extends over a surface substantially corresponding to the surface of development of said belt structure (6). Alternatively, said layer (9) extends only along at least one portion of the development of said belt structure (6), for instance at opposite side portions of said belt structure (6) (not represented in Fig. 1).

In the case of tubeless tyres, a rubber layer (not shown in Fig 1) generally known as a "liner", which provides the necessary impermeability to the inflation air of the tyre, may also be provided in a radially internal position relative to the carcass ply (3).

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Fig. 2 show the same tyre (1) of Fig. 1 the only difference being the fact that a layer of a crosslinked elastomeric material (9) according to the present invention is interposed between the tread band (8) and the belt structure (6). In Fig. 2, said layer (9) extends over a surface substantially corresponding to the surface of development of said belt structure (6). Alternatively, said layer (9) extends only along at least one portion of the development of said belt structure (6), for instance at opposite side portions of said belt structure (6) (not represented in Fig. 2). Alternatively, a further layer of a crosslinked elastomeric material according to the present invention is placed between the belt structure (7) and the carcass ply (3) (not represented in Fig. 2).

The process for producing the tyre according to the present invention may be carried out according to techniques and using apparatus that are known in the art, as described, for example, in patents EP 461 646 and EP 718 122, said process including at least one step of manufacturing the green tyre and at least one step of vulcanizing this tyre.

More particularly, the process for producing the tyre comprises the steps of preparing, beforehand and separately from each other, a series of semi-finished products corresponding to the various parts of the tyre (carcass plies, belt structure, bead wires, fillers, side walls and tread band) which are then combined together using a suitable manufacturing machine. Next, the subsequent vulcanization step welds the abovementioned semi-finished products together to give a monolithic block, i.e. the finished tyre.

The step of preparing the abovementioned semi-finished products will be preceded by a step of preparing and moulding the various blends, of which said semi-finished products are made, according to

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conventional techniques.

The green tyre thus obtained is then passed to the subsequent steps of moulding and vulcanization. To this end, a vulcanization mould is used which is designed to receive the tyre being processed inside a moulding cavity having walls which are countermoulded to define the outer surface of the tyre when the vulcanization is complete.

Alternative processes for producing a tyre or parts of a tyre without using semi-finished products are disclosed, for example, in the abovementioned European Patent EP 976 536 and International Patent Application WO 01/54926.

The green tyre may be moulded by introducing a pressurized fluid into the space defined by the inner surface of the tyre, so as to press the outer surface of the green tyre against the walls of the moulding cavity. In one of the moulding methods widely practised, a vulcanization chamber made of elastomeric material, filled with steam and/or another fluid under pressure, is inflated inside the tyre closed inside the moulding cavity. In this way, the green tyre is pushed against the inner walls of the moulding cavity, thus obtaining the desired moulding. Alternatively, the moulding may be carried out without an inflatable vulcanization chamber, by providing inside the tyre a toroidal metal support shaped according to the configuration of the inner surface of the tyre to be obtained as described, for example, in patent EP 242 840. The difference in coefficient of thermal expansion between the toroidal metal support and the crude elastomeric material is exploited to achieve an adequate moulding pressure.

At this point, the step of vulcanizing the crude elastomeric material present in the tyre is carried out. To this end, the outer wall of the vulcanization mould is placed in contact with a heating fluid (generally

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steam) such that the outer wall reaches a maximum temperature generally of between 100°C and 230°C. Simultaneously, the inner surface of the tyre is heated to the vulcanization temperature using the same pressurized fluid used to press the tyre against the walls of the moulding cavity, heated to a maximum temperature of between 100°C and 250°C. The time required to obtain a satisfactory degree of vulcanization throughout the mass of the elastomeric material may vary in general between 3 min and 90 min and depends mainly on the dimensions of the tyre. When the vulcanization is complete, the tyre is removed from the vulcanization mould.

Although the present invention has been illustrated specifically in relation to a tyre, other crosslinked elastomeric manufactured products that may be produced according to the invention may be, for example, conveyor belts, driving belts or flexible tubes.

The present invention will be further illustrated below by means of a number of preparation examples, which are given for purely indicative purposes and without any limitation of this invention.

EXAMPLES 1-3

Preparation of the elastomeric materials

The elastomeric materials given in Table 1 were prepared as follows (the amounts of the various ingredients are given in phr).

All the ingredients, except sulphur, accelerator and retardant, were mixed together in an internal mixer (model Pomini PL 1.6) for about 5 min (1st Step). As soon as the temperature reached 145±5°C, the elastomeric material was discharged. The sulphur, the accelerator and the retardant were then added and mixing was carried out in an open roll mixer (2nd Step).

EXAMPLE 4

Preparation of the elastomeric material

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The elastomeric material given in Table 1 was prepared as follows (the amounts of the various components are given in phr).

5 All the ingredients except sulphur, accelerator and retardant, were fed to a parallel twin-screw (co-rotating) extruder having a length/diameter ratio $L/D = 30$. After a first pre-mixing step (about 5 minutes), the sulphur, the accelerators and the retardant were added to the extruder. The maximum temperature reached during
10 the extrusion was of $150^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The resulting mixture was cooled by water.

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TABLE 1

EXAMPLE	1 (*)	2 (*)	3	4
1 st Step				
NR	100	88.3	100	70
N326	60	60	60	60
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Antioxidant	2	2	2	2
TESPT	-	-	2	2
Kevlar®	-	15.2	-	-
Dellite® 67G	-	-	20	-
Dellite® 67G	-	-	-	20
2 nd Step				
TBBS	1.6	1.6	1.6	1.6
Sulphur	3.5	3.5	3.5	3.5
PVI	0.3	0.3	0.3	0.3

(*) : comparative.

5 NR: natural rubber;

N326: carbon black;

Antioxidant: phenyl-p-phenylenediamine;

TESPT: bis(3-triethoxysilylpropyl)tetrasulfide (X50S
comprising 50% of carbon black and 50% of silane -10 Degussa-Hüls - the reported amount relates to the
silane amount);Kevlar® Engineered Elastomer: blend of 23% by weight of
Kevlar® and 77% by weight of natural rubber
(DuPont);

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Dellite® 67G: organo-modified montmorillonite belonging to the smectite family (Laviosa Chimica Mineraria S.p.A.);

PVI (retardant): N-cyclohexylthiophthalimide

5 (Santogard® PVI - Monsanto).

The Mooney viscosity ML(1+4) at 100°C was measured, according to ISO standard 289/1, on the non-crosslinked materials obtained as described above. The results obtained are given in Table 2.

10 The static mechanical properties according to ISO standard 37 were measured at different elongation (10%, 50% 100% and 300%) both in the direction of calendaring and in the direction perpendicular thereto on samples of said elastomeric materials crosslinked at 170°C for 10

15 minutes. The result obtained are given in Table 2. Also given in Table 2 are the hardness in IRHD degrees at 23°C and at 100°C according to ISO standard 48 which were measured on samples of said elastomeric materials crosslinked at 150°C for 30 minutes.

20 Table 2 also shows the dynamic mechanical properties measured using an Instron dynamic device in the traction-compression mode according to the following methods. A test piece of the crosslinked material having a cylindrical form (length = 25 mm; diameter = 14 mm)

25 compression-preloaded up to 10% longitudinal deformation with respect to the initial length and kept at the prefixed temperature (23°C and 70°C) for the whole duration of the test, was submitted to a dynamic sinusoidal strain with an amplitude $\pm 3.33\%$ with respect

30 to the length under pre-load, with a frequency of 100 Hz. The dynamic mechanical properties are expressed in terms of dynamic elastic modulus (E') and $\tan \delta$ (loss factor) values. As is known, the $\tan \delta$ value is calculated as a ratio between the viscous modulus (E'')

35 and the elastic modulus (E'), both of them being determined with the above dynamic measurements.

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TABLE 2

EXAMPLE	1 (*)	2 (*)	3	4
Viscosity ML (1+4)	73.0	55.2	68.7	65.9
STATIC MECHANICAL PROPERTIES				
DIRECTION OF CALENDERING				
10% Modulus (MPa)	1.39	3.00	3.43	3.14
50% Modulus (MPa)	2.70	8.62	6.28	5.90
100% Modulus (MPa)	4.53	10.03	10.33	9.58
300% Modulus (MPa)	17.26	19.08	24.00	23.06
Stress at break (MPa)	23.61	19.52	24.07	24.83
DIRECTION PERPENDICULAR TO CALENDERING				
10% Modulus (MPa)	1.33	1.76	3.17	2.88
50% Modulus (MPa)	2.52	3.88	5.94	5.21
100% Modulus (MPa)	4.18	6.14	9.78	8.43
300% Modulus (MPa)	16.63	16.02	23.51	20.99
Stress at break (MPa)	23.00	17.45	23.74	22.40
DYNAMIC MECHANICAL PROPERTIES				
E' (23°C)	17.81	22.51	51.40	42.03
E' (70°C)	14.70	17.55	38.97	32.87
Tan delta (23°C)	0.2098	0.2036	0.2912	0.2985
Tan delta (70°C)	0.1529	0.1488	0.2372	0.2377
IRHD hardness at 23°C	90.60	90.30	95.25	95.90
IRHD hardness at 100°C	82.20	88.00	89.90	89.90

(*) : comparative.

The results given in Table 2 show that the layered inorganic material according to the present invention (Examples 3 and 4) gives both a longitudinal and a transversal reinforcement to the elastomeric material. In particular, a transversal reinforcement is higher than transversal reinforcement given by Kevlar® (Example 2).

d-spacing measurement

Using the elastomeric materials obtained in Examples

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3 and 4, thin films with thickness of 100 μm were prepared by moulding for 5 minutes at 140°C and at 200 bar.

5 The films thus obtained were submitted to X-ray diffraction analysis using a Philips Xpert diffractometer and operating as described above. The following d-spacing values were obtained:

- Sample of Example 3 = 41.09 Å;
- Sample of Example 4 = 40.15 Å.

10 These values, when compared with the d-spacing value of Dellite® 67G in powder form, which was equal to 32.1 Å, show that intercalation of the diene elastomeric polymer in the layered inorganic material had occurred: in fact, a change in d-spacing value was obtained, equal
15 to 28% for Sample of Example 3 and to 25% for Sample of Example 4.

EXAMPLES 5-6

Evaluation of the performance qualities on the road

20 Tyres according to Fig. 1 were prepared containing layers of elastomeric material according to Example 2 (Example 5 - reference) and according to Example 3 (Example 6 - according to the present invention) extending over a surface substantially corresponding to the surface of development of the zero-degree belt
25 structure.

The obtained tyres of 180/55 R17 size, were mounted on a BMW touring motorcycle and tested on a racing circuit: the obtained results are given in Table 3.

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TABLE 3

EXAMPLE	5 (*)	6
Handling	ref.	better than ref.
Directional stability	ref.	better than ref.
Curve roadholding	ref.	much better than ref.
Cornering speed	ref.	much better than ref.
Wear uniformity	ref.	better than ref.

(*): reference.

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CLAIMS

1. Tyre for two-wheeled vehicles, comprising:
- 5 a carcass structure with at least one carcass ply shaped in a substantially toroidal configuration, the opposite lateral edges of which are associated with respective right-hand and left-hand bead wires, each bead wire being enclosed in a respective bead;
 - 10 a belt structure applied in a circumferentially external position relative to said carcass structure;
 - a tread band superimposed circumferentially on said belt structure;
 - 15 a pair of side walls applied laterally on opposite sides relative to said carcass structure;
- wherein said belt structure is associated with at least one layer of a crosslinked elastomeric material comprising:
- 20 (a) at least one diene elastomeric polymer;
 - (b) at least one layered inorganic material having an individual layer thickness of from 0.01 nm to 30 nm.
- 25 2. Tyre for two-wheeled vehicles according to claim 1, wherein said at least one layered inorganic material has an individual layer thickness of from 0.05 nm to 15 nm.
- 30 3. Tyre for two-wheeled vehicles according to claim 1, wherein said layered inorganic material is intercalated in the elastomeric material.
4. Tyre for two-wheeled vehicles according to claim 1, wherein said layered inorganic material is exfoliated in the elastomeric material.
- 35 5. Tyre for two-wheeled vehicles according to claim 1, wherein said layered inorganic material (b)

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- exhibits, in the elastomeric material, a d-spacing value in X-ray diffraction analysis of at least 10% higher with respect to the d-spacing value of the layered inorganic material (b) before dispersing it into the diene elastomeric polymer (a).
- 5 6. Tyre for two-wheeled vehicles according to claim 5, wherein said layered inorganic material (b) exhibits, in the elastomeric material, a d-spacing value in X-ray diffraction analysis of at least 20% higher with respect to the d-spacing value of the layered inorganic material (b) before dispersing it into the diene elastomeric polymer (a).
- 10 7. Tyre for two-wheeled vehicles according to claim 1, wherein said belt structure comprises at least one layer of a plurality of circumferential coils, axially arranged side by side, of at least one cord wound at substantially-null angle with respect to the equatorial plane of the tyre.
- 15 8. Tyre for two-wheeled vehicles according to claim 1, wherein said belt structure comprises two layers of cords oriented according to two preferred directions crossing each other in the two layers and preferably symmetrically inclined in relation to the equatorial plane of the tyre.
- 20 9. Tyre for two-wheeled vehicles according to claim 1, wherein said belt structure comprises a combination of the structure according to claim 7 with the structure according to claim 8.
- 25 10. Tyre for two-wheeled vehicles according to claim 1, wherein said at least one layer of a crosslinked elastomeric material is placed between said carcass structure and said belt structure.
- 30 11. Tyre for two-wheeled vehicles according to claim 1, wherein said at least one layer of a crosslinked elastomeric material is placed between said tread band and said belt structure.
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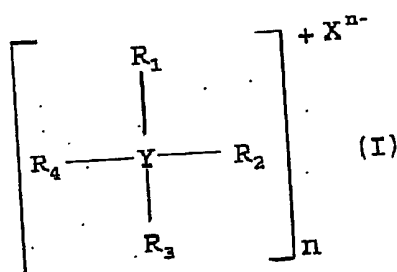
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12. Tyre for two-wheeled vehicles according to any one of the preceding claims, wherein said layer of elastomeric material has a thickness of between 0.075 mm and 5 mm.
- 5 13. Tyre for two-wheeled vehicles according to claim 12, wherein said layer of elastomeric material has a thickness of between 0.4 mm and 3 mm.
- 10 14. Tyre for two-wheeled vehicles according to any one of the preceding claims, wherein the layered inorganic material (b) is present in the elastomeric material in an amount of from 1 phr to 120 phr.
- 15 15. Tyre for two-wheeled vehicles according to claim 14, wherein the layered inorganic material (b) is present in the elastomeric material in an amount of from 5 phr to 80 phr.
- 20 16. Tyre for two-wheeled vehicles according to any one of the preceding claims, wherein the layered inorganic material (b) is selected from phyllosilicates such as: smectites, such as, montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite; vermiculite; halloisite; sericite; or mixtures thereof.
- 25 17. Tyre for two-wheeled vehicles according to claim 16, wherein the layered inorganic material (b) is montmorillonite.
18. Tyre for two-wheeled vehicles according claim 16 or 17, wherein the layered inorganic material (b) is surface-treated with a compatibilizer.
- 30 19. Tyre for two-wheeled vehicles according to claim 18, wherein the compatibilizer is selected from the quaternary ammonium or phosphonium salts having general formula (I):

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wherein:

- Y represents N or P;
 - R_1 , R_2 , R_3 and R_4 , which may be identical or different, represent a linear or branched C_1 - C_{20} alkyl or hydroxyalkyl group; a linear or branched C_1 - C_{20} alkenyl or hydroxyalkenyl group; a group $-R_5-SH$ or R_5-NH wherein R_5 represents a linear or branched C_1 - C_{20} alkylene group; a C_6 - C_{18} aryl group; a C_7 - C_{20} arylalkyl or alkylaryl group; a C_5 - C_{18} cycloalkyl group, said cycloalkyl group possibly containing hetero atom such as oxygen, nitrogen or sulphur;
 - X^{n-} represents an anion such as the chlorine ion, the sulphate ion or the phosphate ion;
 - n represents 1, 2 or 3.
20. Tyre for two-wheeled vehicles according to any one of the preceding claims, wherein the diene elastomeric polymer (a) has a glass transition temperature (T_g) below $20^\circ C$.
21. Tyre for two-wheeled vehicles according to claim 20, wherein the diene elastomeric polymer (a) is selected from: cis-1,4-polyisoprene, 3,4-polyisoprene, polybutadiene, optionally halogenated isoprene/isobutene copolymers, 1,3-butadiene/acrylonitrile copolymers, styrene/1,3-butadiene copolymers, styrene/isoprene/1,3-butadiene copolymers, styrene/1,3-butadiene/acrylonitrile copolymers, or mixtures thereof.
22. Tyre for two-wheeled vehicles according to any one of the preceding claims, wherein the elastomeric

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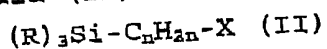
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material comprises at least one elastomeric polymer of one or more monoolefins with an olefinic comonomer or derivatives thereof (a').

- 5 23. Tyre for two-wheeled vehicles according to claim 22, wherein the elastomeric polymer (a') is selected from: ethylene/propylene copolymers (EPR) or ethylene/propylene/diene copolymers (EPDM); polyisobutene; butyl rubbers; halobutyl rubbers; or mixtures thereof.

- 10 24. Tyre for two-wheeled vehicles according to any one of the preceding claim, wherein the elastomeric material further comprises at least one silane coupling agent (c).

- 15 25. Tyre for two-wheeled vehicles according to claim 24, wherein the silane coupling agent (c) is selected from those having at least one hydrolizable silane group which may be identified by the following structural formula (II):



- 20 in which the groups R, which may be identical or different, are selected from: alkyl, alkoxy or aryloxy groups or from halogen atoms, on condition that at least one of the groups R is an alkoxy or aryloxy group; n is an integer between 1 and 6 inclusive; X is a group selected from: nitroso, mercapto, amino, epoxide, vinyl, imide, chloro,
- 25 $-(S)_mC_nH_{2n}-Si-(R)_3$ in which m and n are integers between 1 and 6 inclusive and the groups R are defined as above.

- 30 26. Tyre for two-wheeled vehicles according to claim 24 or 25, wherein the silane coupling agent (c) is present in the elastomeric material in an amount of from 0.01 phr to 10 phr.

- 35 27. Tyre for two-wheeled vehicles according to claim 26, wherein the silane coupling agent (c) is present in an amount of from 0.5 phr to 5 phr.

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28. Tyre for two-wheeled vehicles according to any one of the preceding claims, wherein at least one additional reinforcing filler is present in an amount of between 0.1 phr and 120 phr in the elastomeric material.
29. Tyre for two-wheeled vehicles according to claim 28, wherein the reinforcing filler is carbon black.
30. Tyre for two-wheeled vehicles according to claim 28, wherein the reinforcing filler is silica.
31. Tyre for two-wheeled vehicles according to claim 30, wherein at least one silane coupling agent (c) is present.
32. Process for producing a tyre for two-wheeled vehicles, said process comprising the following steps:
- manufacturing a green tyre by assembling at least one carcass ply, a belt structure in a circumferentially outer position with respect to said carcass ply, a tread in a circumferentially outer position with respect to said belt structure;
 - subjecting the green tyre to moulding in a mould cavity formed in a vulcanization mould;
 - subjecting said green tyre to crosslinking by heating;
- said process further comprising the step of associating at least one layer of a crosslinkable elastomeric material with said belt structure, said elastomeric material comprising:
- (a) at least one diene elastomeric polymer;
 - (b) at least one layered inorganic material having an individual layer thickness of from 0.01 nm to 30 nm.
33. Process according to claim 32, wherein said at least one layered inorganic material has an individual layer thickness of from 0.05 nm to 15 nm.

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34. Process according to claim 32 or 33, wherein said layered inorganic material is intercalated in the elastomeric material.
- 5 35. Process according to any one of claim 32 or 34, wherein said layered inorganic material is exfoliated in the elastomeric material.
36. Process according to any one of claims 32 to 35, wherein said layer of elastomeric material has a thickness of between 0.075 mm and 5 mm.
- 10 37. Process according to claim 36, wherein said layer of elastomeric material has a thickness of between 0.4 mm and 3 mm.
- 15 38. Process according to any one of claims 32 to 37, wherein said layered inorganic material (b) exhibits, in the elastomeric material, a d-spacing value in X-ray diffraction analysis of at least 10% higher with respect to the d-spacing value of the layered inorganic material (b) before dispersing it into the diene elastomeric polymer (a).
- 20 39. Process according to claim 38, wherein said layered inorganic material (b) exhibits, in the elastomeric material, a d-spacing value in X-ray diffraction analysis of at least 20% higher with respect to the d-spacing value of the layered inorganic material (b) before dispersing it into the diene elastomeric polymer (a).
- 25 40. Process according to any one of claims 32 to 39, wherein said at least one layer of crosslinkable elastomeric material is obtained by winding at least one ribbon-like band consisting of said crosslinkable elastomeric material in side by side coils.
- 30 41. Process according to any one of claims 32 to 40, wherein the layered inorganic material (b) is defined according to any one of claims 14 to 19.
- 35 42. Process according to any one of claims 32 to 41,

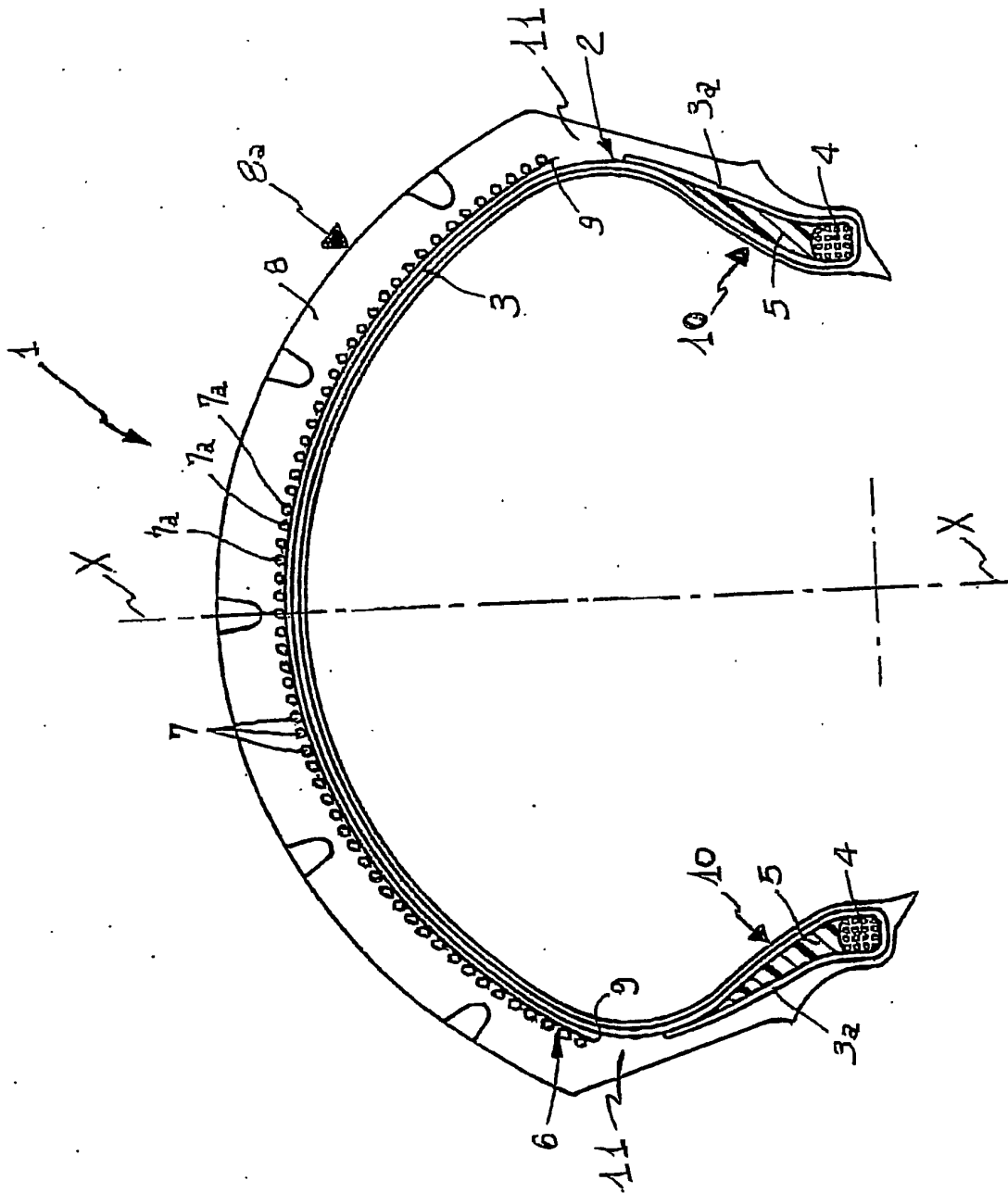
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- wherein the diene elastomeric polymer (a) is defined according to claim 20 or 21.
- 5 43. Process according to any one of claims 32 to 42, wherein the elastomeric material comprises at least one elastomeric polymer of one or more monoclefins with an olefinic comonomer or derivatives thereof (a') as defined according to claim 23.
- 10 44. Process according to any one of claims 32 to 43, wherein the elastomeric composition further comprises at least one coupling agent (c) as defined according to any one of claims 24 to 27.
- 15 45. Process according to any one of claims 32 to 44, wherein at least one additional reinforcing filler is present, in an amount of between 0.1 phr and 120 phr, in the elastomeric composition.
46. Process according to claim 45, wherein the reinforcing filler is carbon black.
47. Process according to claim 45, wherein the reinforcing filler is silica.
- 20 48. Process according to claim 47, wherein at least one silane coupling agent (c) is present.

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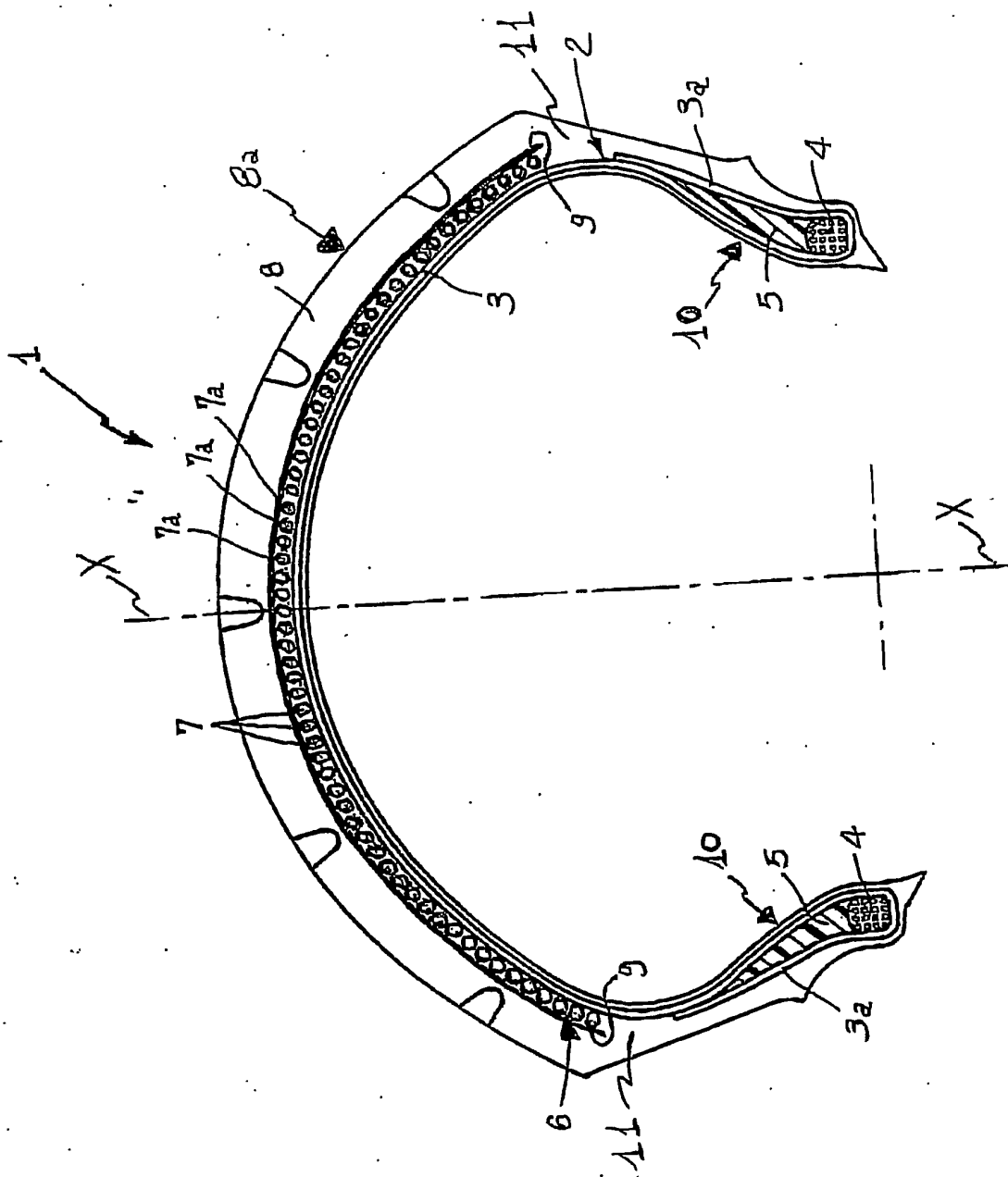


Fig. 2

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